

AFOSR Final Performance Report

FA9550-06-1-0049

Spectroscopic Characterization of Reactive Intermediates Relevant to Supersonic Combustion

Mark A. Johnson
Department of Chemistry
Yale University
P.O. Box 208107
New Haven, CT

28 February 2009

I. Status of Effort

Our program specializes in the spectroscopic characterization of molecular ions and reactive intermediates in ion-molecule reactions, and is closely integrated with ongoing activities at the AFRL Space Vehicles Directorate to determine the temperature dependence of ion-molecule and ion-ion reaction kinetics which are important in high-velocity (*e.g.*, scramjet) combustion and re-entry plasma. We also interact with parallel AFOSR-sponsored theoretical programs that build predictive models based on both *ab initio* and scattering approaches. Our role in this collaboration is to provide experimental benchmarks for bond energies, structures (*e.g.*, CO_3^- , SF_6^- , POCl_3^- , PO_3^-), and stationary points in the potential energy profiles for reactions ($\text{O}_2^+ + \text{CH}_4$, $\text{O}^- + \text{CH}_2\text{CH}_2$, $\text{HCCH}^+ + \text{HCCH}$) that are relevant models for ion-assisted combustion of hydrocarbons. Here we describe the results of our first AFOSR grant supporting this endeavor. We first review the methods used to carry out the measurements, and then discuss specific results obtained out with this experimental approach.

20090429226

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-09-0137

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden suggestions for reducing the burden, to the Department of Defense, Executive Service Directorate (0704-0188). Respondents should be aware that this person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) 29-02-2009	2. REPORT TYPE Final Performance Report	3. DATES COVERED (From - To) January 2006 - November 2008		
4. TITLE AND SUBTITLE Characterization of Reactive Intermediates Relevant to Supersonic Combustion		5a. CONTRACT NUMBER FA9550-06-1-0049		
		5b. GRANT NUMBER FA9550-06-1-0049		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Johnson, Mark, A.		5d. PROJECT NUMBER		
		5e. TASK NUMBER		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Yale University 155 Whitney Avenue P.O. Box 208337 New Haven, CT 06520-8337				
8. PERFORMING ORGANIZATION REPORT NUMBER N/A				
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR 875 N Randolph St Arlington, VA 22203 Dr. Berman/NA				
10. SPONSOR/MONITOR'S ACRONYM(S)				
11. SPONSOR/MONITOR'S REPORT NUMBER(S)				
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution A: Approved for Public Release				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT Our program specializes in the spectroscopic characterization of molecular ions and reactive intermediates in ion-molecule reactions, and is closely integrated with ongoing activities at the AFRL Space Vehicles Directorate to determine the temperature dependence of ion-molecule and ion-ion reaction kinetics which are important in high-velocity (e.g., scramjet) combustion and re-entry plasma. Our role in this collaboration was to provide experimental benchmarks for bond energies, structures (e.g., CO ₃ ⁻ , peroxy nitrite (OONO ⁻ , SF ₆ ⁻ , On ⁻), and stationary points in the potential energy profiles for reactions (O ₂ ⁺ + CH ₄ , O ⁻ + CH ₂ CH ₂ , HCCH ⁺ + HCCH) that are relevant models for ion-assisted combustion of hydrocarbons. Our spectroscopic measurements exploit recently developed Ar cluster-mediated methods for both synthesis and structural characterization of ions using vibrational and (for anions) photoelectron spectroscopies. Significant results from this endeavor include the design and execution of a laser-based method for obtaining bond energies of polyatomic ions. Application of this method to the CO ₃ ⁻ ion revealed that the previously accepted value was in error by 0.5 eV, a sufficiently large correction to qualitatively affect kinetic models involving this species.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF: a. REPORT b. ABSTRACT c. THIS PAGE		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Johnson, Mark, A. 19b. TELEPHONE NUMBER (Include area code) 203-432-5226

II. Experimental approach

Our spectroscopic measurements are based on recently developed Ar cluster-mediated methods for both synthesis and structural characterization of ions using vibrational predissociation and (for anions) photoelectron spectroscopies. In this scheme, the target ion, $\text{AB}^{+/-}$, is synthesized by condensation of a neutral reagent (B) onto an ion (A) embedded in an intermediate sized (10-30 atoms) Ar cluster:



The resulting “tagged” $\text{AB}^+ \cdot \text{Ar}_m$ species is necessarily cold (typically 20-40 K), and its structure can be readily deduced by analysis of its vibrational (or electronic) spectrum obtained using “messenger” spectroscopy:



One cannot overstate the benefits of this combined approach in that i) the ions are cooled

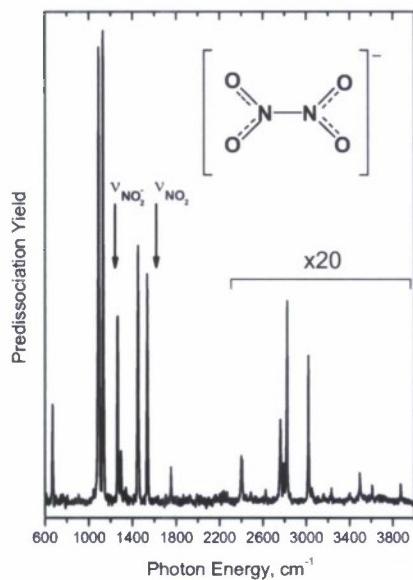


Figure 1: Vibrational predissociation spectrum of the $\text{N}_2\text{O}_4^- \cdot \text{Ar}$ complex. The IR fundamentals of the bare NO_2 and NO_2^- constituents are indicated by arrows.

close to their minimum energy (zero-point) configurations, and ii) the spectra are obtained in a linear action regime. Together, these aspects enable straightforward comparison with theory, and afford general access to labile species like reactive intermediates and high-energy isomers. The recent development of widely applicable synthetic methods, together with the availability of broadly tunable, tabletop laser systems (advances in which we have played a leading role) have dramatically

increased the practical utility of this method. The performance that can now be routinely achieved is illustrated in Fig. 1, where sharp bands are recovered for the N_2O_4^- charge-transfer stabilized dimer over the range 600-4000 cm^{-1} with continuous coverage and high signal-to-noise. The relatively recent extension into the lower-energy ($<2000 \text{ cm}^{-1}$) fingerprint region using AgGaSe_2 as a mixing medium is critical for structurally characterizing ions of greatest interest in this project, which often exclusively involve heavy atoms (O, N, P, Cl, F and C) and thus low-energy fundamentals. We are exploiting this circumstance to solve some of the longest-standing puzzles regarding the structures and thermochemistries of common species relevant to the AFOSR mission. Specifically, our program was able to combine a variety of complementary techniques to resolve several key outstanding issues regarding the behavior of the CO_3^- and SF_6^- ions, for example, which have been largely avoided by the academic ion chemistry community precisely because they were regarded as pathological. We also highlight progress on several other systems presently under study.

The results obtained were acquired on the second-generation tandem time-of-flight (TOF) photofragmentation mass spectrometer that has recently been augmented to include velocity-map photoelectron imaging spectroscopy.

III. Summary of Results

The first targets identified by AFRL as most in need of our attention were the determination of the bond energy of the CO_3^- anion and elucidation of the structure and electron binding energy of the ubiquitous SF_6^- anion. Both ions are notoriously difficult to study in spite of decades of effort on each, partly as a result of the fact that they each undergo very strong structural changes upon detachment of the excess electron. This

scenario inevitably leads to large internal energy content on formation, thus making cooling imperative in order to be sure measurements correspond to ground-state species which can be compared with theory. In both of these cases, cooling was efficiently achieved by Ar attachment, which limits the internal energy content to the order of the Ar binding energy (several hundred wavenumbers).

III A. Electron binding energy and structure of SF₆⁻

The SF₆⁻ anion is of practical importance to the Air Force in the context of mediating electron-rich plasmas associated with high-velocity vehicles and as a fuel additive. SF₆ has been known for decades to have the remarkable ability to absorb slow electrons to form SF₆⁻ even under very low pressure conditions where three-body stabilization is severely suppressed. Qualitatively, it is understood that the strong structural distortion of the anion relative to the neutral is the underlying cause for this property. The anion has resisted structural characterization for all these years, however, because the vibrational fundamentals lie very low in energy, and photoelectron spectroscopy of such strongly distorted systems results in excitation of extremely high vibrational levels in the Franck-Condon region of the neutral (note that this is also true in the case of CO₃⁻, discussed in section IIIB). This, in turn, complicates the usual strategy of

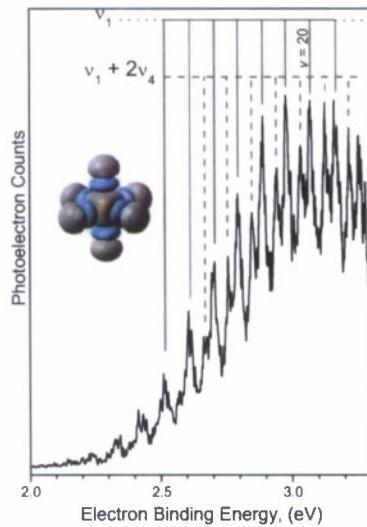


Figure 2: 355 nm photoelectron spectrum of SF₆⁻ · Ar. The predominant vibrational feature is the 750 cm⁻¹ (v_1) symmetric stretch mode (solid lines), while the secondary progression is a combination of v_1 plus two quanta of the triply degenerate v_4 mode (dashed lines) (see *Chem. Phys. Lett.* **445**, 84 (2007)). The inset shows the SF₆⁻ excess electron orbital calculated at the B3LYP/aug-cc-pvdz level of theory.

fitting the vibrational envelopes to recover anion structure. In the SF_6^- case, for example, the calculated vertical detachment energy (3.5 eV) is far above the adiabatic electron affinity estimated from thermochemistry to be around 1.2 eV. The Ar-tagged photoelectron spectrum is reproduced in Fig. 2, which reveals a beautiful vibrational progression in only two modes that extends over approximately one electron volt. To address the possibility that the Ar tag was, in fact, perturbing the system, we engaged a collaboration with the group of AFOSR contractor Prof. W. C. Lineberger, because they have the capability of measuring the photoelectron spectra of bare ions cooled close to liquid N₂ temperatures in a flow tube ion source. The JILA measurements confirmed that the progression observed in the $\text{SF}_6^- \cdot \text{Ar}$ spectrum was, in fact, a property of the cold ions and not an unwanted consequence of the Ar tag.

An interesting result from the analysis of the vibrational progression was that there are two active modes. One of these is the totally symmetric A_{1g} mode, which is expected as a result of the calculated geometry change in the anion that preserves O_h symmetry by a substantial elongation of the S-F bonds (by ~0.2 Å). This results in a peak in the population of the v_1 symmetric stretching mode in the neutral at about $v = 27$. A second mode is also clear as an interloper, and is due to a combination excitation ($v_1 + 2v_4$), that arises from a strong Duschinsky rotation involving mixing between v_1 and the v_3 and v_4 modes upon removal of the electron. For completeness, we also recorded the vibrational predissociation spectrum of the $\text{SF}_6^- \cdot \text{Ar}$ complex, and recovered a single feature at around 620 cm⁻¹ assigned to the degenerate stretching mode, analogous to the strong 948 cm⁻¹ infrared fundamental in SF₆ neutral. This study was combined with a related analysis of the C₄F₈ anion in Ref. [1].

IIIB. Bond energy of CO_3^- using Ar-mediated, resonant two-photon photodissociation

Interest in the CO_3^- anion arises because this species and its hydrates are abundant in Earth's atmosphere and are reagents of choice in chemical ionization mass analysis of engine exhaust. Laboratory measurements involving simple reactions in a flow tube such as:



indicated that several reactions occur quite efficiently even though they are nominally endothermic. This led kineticists to question the accepted dissociation energy of the $\text{CO}_2\text{-O}^-$ bond. We therefore set out to refine the bond energy, and did so with the scheme outlined in Fig. 3. This was an interesting chemical physics challenge, and we tailored our approach to turn the extensive vibronic coupling that has plagued spectroscopists over the years to our advantage. We began by first cooling the system via formation of the $\text{CO}_3^- \cdot \text{Ar}$ complex, and then photoexcited it through the electronic band near 650 nm, which is known to undergo rapid internal conversion to ground state CO_3^- , presumably through a conical intersection. Rapid Ar loss then leads to formation of very hot (~ 1.9 eV), ground-state CO_3^- , which is cooled somewhat by evaporation of the weakly bound Ar atom. The dissociation

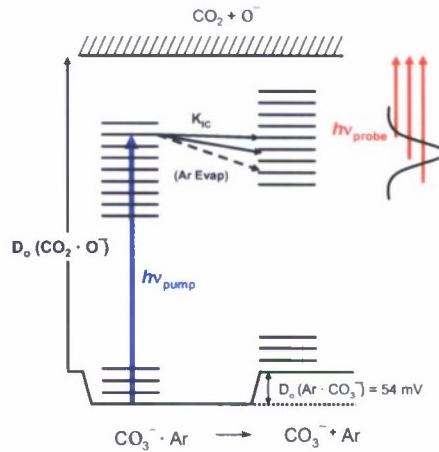


Figure 3: Schematic showing the strategy of the bond energy measurement using two-photon photofragmentation over the threshold. This approach leverages heavily against the extensive vibronic coupling in this system, such that the dissociation threshold can be accessed through unimolecular decomposition of the electronically excited molecule.

threshold was then obtained by scanning a second laser in the neighborhood of 0.7 eV, where the transition moment arises from vibronically induced transitions associated with a nominally dark, low-lying electronic state, based on the behavior of the isoelectronic NO_3 system. This electronic energy is then channeled to the dissociation coordinate after extensive internal energy randomization to yield $\text{CO}_2 + \text{O}^-$ products as a micro-canonical (RRKM) decay process. The resulting product yield as a function of the scanned laser photon energy is presented in Fig. 4, where the relatively rapid onset at 2.79 eV is observed far above the previously accepted bond energy, D_0 , of 2.3 eV, and surprisingly close to that deduced by bracketing its reactivity with reagents whose thermochemistry is well established. The photochemical measurement was refined using several pump-probe wavelength combinations as well as variation of the number of attached Ar atoms as described in detail in Ref. [2]. Higher accuracy is clearly available using precision spectroscopic methods; however, we are not presently pursuing this avenue unless driven to do so by the programmatic needs of the AFRL team.

IIIC. Survey of peroxy forms of common molecular anions

The elements C, N and O form a versatile set of atoms from which to build a large variety of stable molecular anions that survive at room temperature and atmospheric pressure. Some species, like the nitrate ion, NO_3^- , are familiar from elementary aqueous

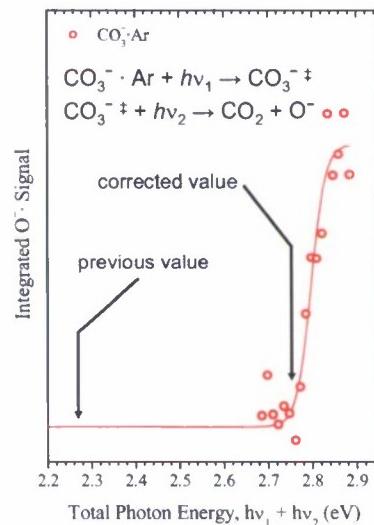


Figure 4: Dissociation threshold measured by scanning the second laser ($h\nu_{\text{probe}}$ in Fig. 3) and monitoring the onset of photofragmentation. The previous value is actually an estimate based on photofragment recoil energy analysis.

chemistry, and are among the most abundant anions in the D-region of the atmosphere. The propensity of these first-row atoms to engage in multiple covalent bonds, however, creates a variety of bonding scenarios varying from fully covalent, charge-delocalized species like NO_3^- to ion-molecule complexes where the constituents retain their original parentage. In the condensed phase, for example, peroxy nitrite (OONO^-), a high-energy isomer of nitrate, plays a central role in biological processes such as aging and Alzheimer's disease. Our goal here was to complement recent work at the AFRL ion lab on kinetics of peroxy nitrite reactions in the gas-phase. We carried out a survey of the structures of a series of peroxy isomers of simple molecules present in the atmosphere ($\text{O}_2^- \cdot \text{CO}_2$, OONO^- , $\text{O}_2^- \cdot \text{O}_2$, $\text{O}_2^- \cdot \text{SO}_2$, $\text{O}_2^- \cdot \text{N}_2$) as well as the $\text{O}_2^- / \text{O}_4^- \cdot$ benzene complexes (Refs. [3-6]) in order to establish the range of their behaviors. The peroxy forms were isolated using the Ar-mediated condensation approach:



where rapid Ar evaporation traps high-energy isomers if significant barriers separate them from the canonical forms of the ions. Using this technique, the (OONO^- and OOCO^-) forms could be selectively prepared and separated from the familiar D_{3h} species.

Fig. 5 compares the spectra of OONO^- (top) and NO_3^- (bottom), while Fig. 6 pertains to OOCO^- (top) and CO_3^- (bottom). Note that the spectra of the two forms are completely exclusive in each case, indicating the isomers can be selectively prepared and

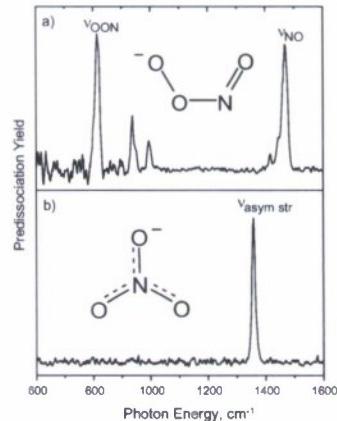


Figure 5: Vibrational predissociation spectra of peroxy nitrite (a) where the two largest features are assigned to the OON and NO stretches, and the D_{3h} nitrate ion (b) which displays only a single asymmetric stretching feature as expected for a molecule with such high symmetry.

studied in high yield. The harmonic predictions are quite good for the NO_3^- and OOCO^- ions, where simple spectra are readily assigned to the degenerate NO stretch and the more or less independent OO^- and CO stretches in the rather distant diatomic moieties in OOCO^- . The OONO^- spectrum is more complex, and may arise from the contribution of the *cis*- and *trans*- isomeric forms. We are presently working with Prof. John Stanton at the University of Texas, Austin, to work out the assignments of the bands in the context of the structures.

In this class of polyoxygencated molecular anions, the nominally D_{3h} form of CO_3^- presents the biggest challenge, as the *ab initio* harmonic prediction completely fails to capture the character of the spectrum displayed in Fig. 6b. The extended spectral range

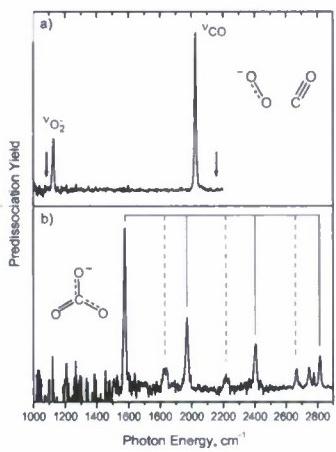


Figure 6: Vibrational predissociation spectra of the $\text{O}_2^- \cdot \text{CO}$ ion-molecule complex (a) which displays two sharp bands very close in energy to the O_2^- and CO fundamentals (arrows), and the CO_3^- molecular ion (b) whose complex electronic structure leads to two progressions built off the main feature at 1575 cm^{-1} , presumably due to strong vibronic interaction with low lying electronic states.

in this scan clarified a confusing situation raised in our first report, (Ref. [2] which had a large gap in coverage. The high-energy bands are now seen to be members of a long, regular progression of two modes based on a fundamental at about 1575 cm^{-1} . In fact, the band structure appears much more like the vibrational manifold associated with electronic excitation to an excited state with a significant geometry change along two normal modes. This unusual behavior appears to reflect the strong distortions of the ground state induced by vibronic coupling with low-lying excited states, as has been recently uncovered in the isoelectronic, and

atmospherically relevant NO_3 radical. A full discussion of the peroxy isomers is presented in Refs. [3, 4, 5, and 6].

IIID. Trapping and characterization of reactive intermediates in ion-molecule reactions

In most applications, ion concentrations are so small that ion-molecule reactions are not relevant to performance optimization. However, when considering combustion in very high velocity engines, (*e.g.* ramjet and scramjet) where reactions must occur on extremely short timescales to deliver thrust, we are presented with an important exception to this rule because these reactions are barrierless and feature high cross sections due to long-range attraction. As such, there is significant effort underway to understand ion-assisted hydrocarbon oxidation. The complexity of these processes is impressive, as can be appreciated by inspection of the calculated reaction profile of the “simple” $\text{CH}_4 + \text{O}_2^+$ reaction displayed in Fig. 7. One of our goals in this program is to identify stationary points along the myriad of curve crossings and locally stable minima on the hypersurface.

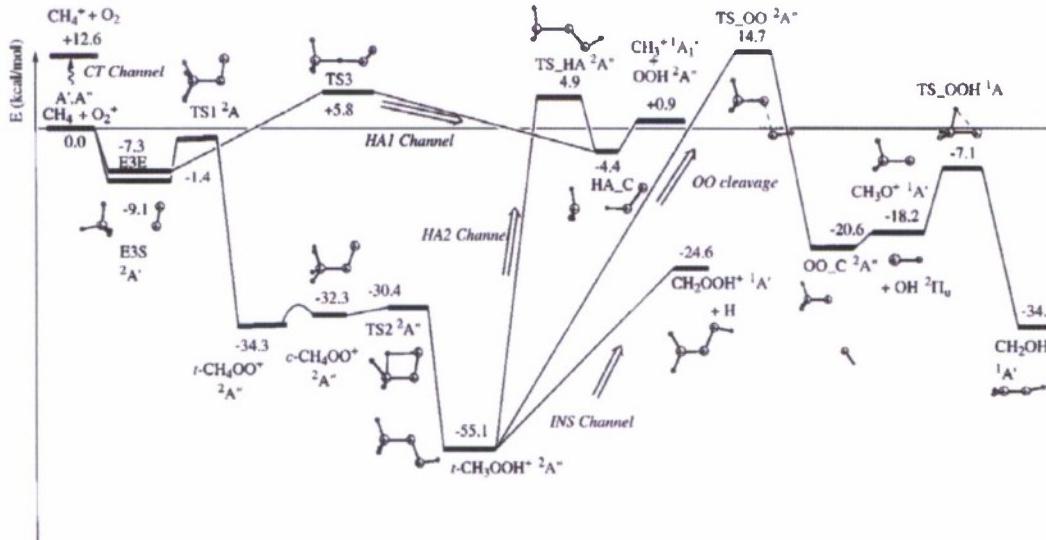
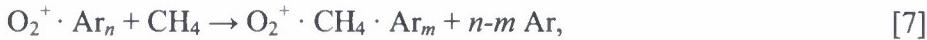


Figure 7: Calculated reaction scheme highlighting the numerous intermediate structures in the reaction $\text{CH}_4 + \text{O}_2^+ \rightarrow \text{CH}_2\text{OH}^+ + \text{OH}$. The Ar-mediated collision scheme (Eq. [7]) traps the entrance channel complex, CH_4O_2^+ (circled in red) at -7.3 kcal/mol in the upper left. Figure reproduced from Irle, S. and Morokuma, K. *J. Chem. Phys.* **114**, 6119 (2001).

Our approach exploits the unique opportunities afforded by coordinating Ar-mediated synthesis and spectroscopy with photoinitiated reactivity measurements. In this grant period, we surveyed the behavior of several archetypal reactions involving hydrocarbons and are therefore in an excellent position to anticipate fruitful directions as well as roadblocks that will need to be overcome in continuing work. The $O_2^+ + CH_4$, $O^- + CH_4$, and $O^- + C_2H_4$ reactions provide clear examples where Ar-mediated condensation fortuitously leads to only one intermediate along the reaction profile (the entrance channel in $O_2^+ + CH_4$ and exit channels in the O^- reactions).

In the $O_2^+ + CH_4$ reaction, we isolated the species formed in the Ar-mediated binary collision:



and characterized its vibrational spectrum, with the result displayed in Fig. 8. We are presently engaged in analyzing the assignments using anharmonicity-corrected (at third order) calculations of the vibrational eigenstructure, but even without these assignments, we can explore aspects of the preparation and qualitatively locate barriers. Once the vibrational resonances are known, for example, photoexcitation of the bare complexes through these transitions reveals whether the intermediate passes over the barrier to reaction or decomposes back into reactants as

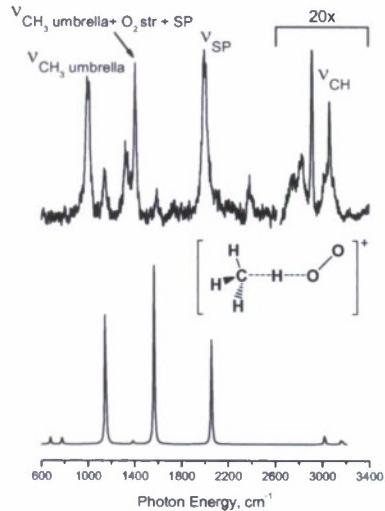


Figure 8: Preliminary argon predissociation spectrum of $CH_4OO^+ \cdot Ar$ is displayed on the top, with a calculated (B3LYP/6-311++g(d,p)) spectrum displayed below. Tentative assignments are shown for the shared proton (SP) motion and other C-H vibrational modes.

illustrated in Fig. 9. A preliminary investigation of the bare complex found that photoactivation in the region of the C-H stretching vibrations at 2900 cm^{-1} leads primarily to decomposition:



with a minor channel ($\sim 10\%$) yielding the $\text{CH}_3\text{OO}^+ + \text{H}$ reaction product. This indicates that the barrier to reaction probably lies close to or even above the dissociation energy back to reactants. Note that the fact that this trapped intermediate can be photodissociated at 2900 cm^{-1} verifies that it is indeed the entrance channel complex, as the only other intermediate with high potential energy is the C-H insertion species CH_3OOH^+ , which would dissociate to $\text{CH}_3^+ + \text{OOH}$ (see Fig. 7). The clear direction for this study is to define the precise location of the barrier relative to the entrance channel dissociation asymptote. This will be achieved by monitoring the CH_3OO^+ vs. O_2^+

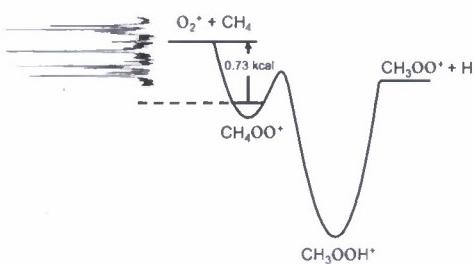


Figure 9: Simplified potential energy diagram of the $\text{O}_2^+ + \text{CH}_4$ reaction pathway. The infrared spectrum obtained from the Ar tagged complex is shown on the left of the potential surface. Excitation of these vibrations yields access to the barriers for product formation and dissociation back to reactants.

photoproduct branching ratio upon excitation of the various bands of the bare complex that were identified using Ar-tagging. The range of energies accessible is indicated by the overlay of the spectrum with the potential energy profile of the reaction in Fig. 9.

III.E. Development of isomer-selective spectroscopy and pump-probe photochemical interconversion of isomers

The complexity of ion-molecule reaction systems such as that depicted in Fig. 7 indicate that the Ar trapping scheme should generally prepare several isomers of a given mass that correspond to isolation of various intermediates. While this provides valuable information about the reaction path, it also creates difficulties in assigning the observed vibrational bands to specific isomers when their contributions overlap in congested regions of the spectrum. Once these contributions have been disentangled, it would then be desirable to measure the relative energies of the minima and the transition state energies separating them. Therefore, midway through this grant period, we set out to develop a hole-burning scheme modeled after the popular resonant ion dip infrared spectroscopy (RIDIRS) technique and its population-transfer variant. Our technique is unique in that it is generally applicable to ionic systems which do not possess the low-lying electronic band system required for RIDIRS, thus allowing us to study the hydrated ion clusters of interest here. Our approach came on-line in the summer of 2008, and is based entirely on Ar-tagging and excitation within the vibrational manifolds.

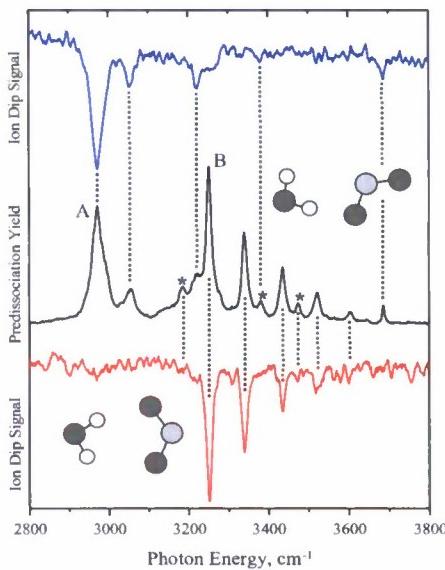


Figure 10: Isomer-selective predissociation spectra of $\text{NO}_2^- \cdot \text{H}_2\text{O} \cdot \text{Ar}$. The ion dip spectra (top and bottom) were obtained by fixing the probe laser on transitions labeled A and B, respectively. Asterisks denote peaks whose assignments were confirmed using fixed-point, laser on-laser off averaging.

Our isomer-specific spectroscopy method capitalizes on the destructive nature of

predisociation to first remove population from the particular isomers that undergo resonant excitation with a powerful, scanning IR laser (pump). An intermediate stage of mass selection is used to separate the photofragments produced in the first predisociation event from the non-dissociated parent ions. These parent ions are subsequently interrogated, again using vibrational predisociation, but with a second IR laser (probe) fixed at a specific transition. The performance of the approach is illustrated by its application to the binary $\text{NO}_2^- \cdot \text{H}_2\text{O}$ complex in Fig. 10, described in Ref. [7]. The non-isomer-selective action spectrum is shown in the middle trace, while the top and bottom traces were generated by fixing the probe laser on the transitions labeled A and B and scanning the powerful pump laser through the vibrational resonances. Two very different spectra are obtained depending on which transition is probed, revealing the presence of two isomers with the structures (top: backside; bottom: frontside) indicated in the insets.

Having defined the presence and spectral signatures of two isomers, we then followed the Ar-cluster mediated photoisomerization between the two forms of the $\text{NO}_2^- \cdot \text{H}_2\text{O}$ complex. The results of this exercise are shown in Fig. 11, where we photoexcited the backside isomer through its OH stretching vibration near 3000 cm^{-1} . The isomerization yield in the photofragment ions could then be determined by monitoring the

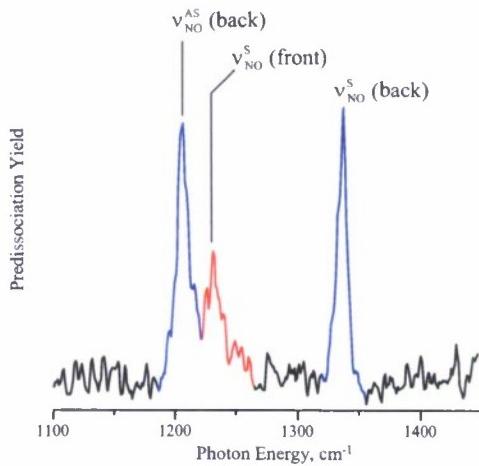


Figure 11: Isomer conversion spectra obtained by pumping $\text{NO}_2^- \cdot \text{H}_2\text{O}$ on the OH stretch of the backside isomer near 3000 cm^{-1} . The appearance of the frontside NO stretch at 1230 cm^{-1} indicates successful conversion of the backside isomer to the frontside form.

relative intensities of their closely spaced NO stretching vibrations near 1200 cm^{-1} . Significant population in the frontside isomer is observed by the weak shoulder at 1230 cm^{-1} , just above the strong band due to the backside form at 1203 cm^{-1} . This is an important observation because reaction path calculations by Prof. Kenneth Jordan indicate that the height of the barrier to isomerization is about 1000 cm^{-1} , which is about *twice* the Ar binding energy. The observation that isomerization can be efficient when it occurs over a higher barrier than that required for Ar loss is in itself interesting. As such, one has access to a microscopic system in which barrier crossing can be followed in the presence of a dissipative solvent. Further details about this aspect of the project are included in Ref. [8].

Publications acknowledging AFOSR support resulting from this grant

1. "Spectroscopic characterization of the isolated SF_6^- and C_4F_8^- anions: Observation of very long harmonic progressions in symmetric deformation modes upon photodetachment," Joseph C. Bopp, Joseph R. Roscioli, Mark A. Johnson, T. M. Miller, A. A. Viggiano, S. M. Villano, S. W. Wren, and W. C. Lineberger, *J. Phys. Chem. A*, **111**, 1214-1221, 2007.
2. "Determination of the CO_3^- Bond Strength via the Resonant Two-Photon Photodissociation Threshold: Electronic and Vibrational Spectroscopy of $\text{CO}_3^- \cdot \text{Ar}_n$," Joseph C. Bopp, Eric G. Diken, Jeffrey M. Headrick, Joseph R. Roscioli, Mark A. Johnson, Anthony J. Midey, and A. A. Viggiano, *J. Chem. Phys.*, **124**, 174302, 2006.
3. "Argon cluster-mediated isolation and vibrational spectra of peroxy and nominally D_{3h} isomers of CO_3^- and NO_3^- ," Rachael A. Relph, Joseph C. Bopp, and Mark A. Johnson, *J. Chem. Phys.*, **129**, 064305, 2008.
4. "Vibrational predissociation spectra of the O_n^- , $n = 3 - 10, 12$ clusters: Even-odd alternation in the core ion," Joseph C. Bopp, Anastassia N. Alexandrova, Ben M. Elliott, Tobias Herden, and Mark A. Johnson, International Journal of Mass Spectrometry, In Press
5. "Kinetics for the Reactions of O^- and O_2^- with $\text{O}_2(\text{a}^1\Delta_g)$ Measured in a Selected Ion Flow Tube at 300 K," Anthony Midey, Itzhak Dotan, S. Lee, W. T. Rawlins, Mark A. Johnson, and A. A. Viggiano, *J. Phys. Chem. A*, **111**, 5218 (2007).
6. "Theoretical and infrared spectroscopic investigation of the O_2^- -benzene and O_4^- -benzene complexes," Holger Schneider, J. Mathias Weber, Evgeniy M. Myshakin, Kenneth D. Jordan, Joseph Bopp, Tobias Herden and Mark A. Johnson, *J. Chem. Phys.*, **127**, 084319 (2007).

7. "Isolating the spectra of cluster ion isomers using Ar-“tag”-mediated IR-IR double resonance within the vibrational manifolds: Application to $\text{NO}_2^-\cdot\text{H}_2\text{O}$,"
Ben M. Elliott, Rachael A. Relph, Joseph R. Roscioli, Joseph C. Bopp, George H. Gardenier, Timothy L. Guasco, Mark A. Johnson, *J. Chem. Phys.*, **129**, 094303, 2008.
8. "Vibrationally-induced interconversion of H-bonded $\text{NO}_2^-\cdot\text{H}_2\text{O}$ isomers within $\text{NO}_2^-\cdot\text{H}_2\text{O}$ Ar_m clusters using IR-IR pump-probe through the OH and NO stretching vibrations,"
Rachael A. Relph, Ben M. Elliott, Gary H. Weddle, Mark A. Johnson, Jing Ding and Kenneth D. Jordan, *J. Phys. Chem. A.*, **113** (6), 975-981, 2009.

Personnel Supported by this grant:

Graduate Students:

Rachael Relph (4th year)
Ben Elliott (4th year)
Mike Kamrath (2nd year)

Post-doctoral associates:

Dr. Laura McCunn (Now Asst. Prof. Marshall University)

Joseph Bopp carried out the major experiments involving structure and energetic determinations of CO_3^- and SF_6^- . In addition, Joe spent a summer as an Air Force Scholar in the ion kinetics laboratories at Hanscom under the direction of Al Viggiano, resulting in an independent paper for Joe that is related to this work. More recently, Rachael Relph has taken over the project with Mike Kamrath, who measured the spectra of peroxyxynitrite and several other peroxy forms of simple ions of relevance to the ion chemistry involved in atmospheric combustion. This team has also made great progress developing hole-burning double resonance as a general method to sort out isomeric contributions to the spectra of complex systems.

Inventions and patent disclosures

There have been no inventions leading to patent disclosures during the period of this grant.

Honors and Awards during grant period

2006 APS Earle K. Plyler Award for Molecular Spectroscopy
2007 Dylan Hixon Award for Teaching Excellence in the Natural Sciences
2008 Yale Science and Engineering Award for Basic and Applied Science

Invited Lectures during grant period

2008
Yale YINQE Seminar
University of California, San Diego (Physical Chemistry Seminar)

University of New Hampshire,
Air Force Office of Scientific Research Contractor's meeting
ACS National Meeting, New Orleans
Keynote Lecture, Beckman Scholar Symposium, Irvine, CA
Conference on Aqueous Solutions and Their Interfaces, Crete, Greece, June 2008
Texas A&M University, (Department Colloquium)
Gordon Conference on Radiation Chemistry (Invited Lecture)
Gordon Conference on Molecular and Ionic Clusters (Session Chair)
Telluride Workshop: Reactions on Multiple Surfaces (Invited Lecture)
Physical Chemistry Symposium for Undergraduate Chemistry Majors, ACS Philadelphia

2007

UCLA Physical Chemistry Seminar
U. Massachusetts, Amherst, Physical Chemistry Seminar
Perspectives in Science (two, April 2007 and November 2007)
Parent's day lecture, Yale University
Gordon Research Conference on gas phase ions, Buelton, CA
International Conference on High Resolution Molecular Spectroscopy, Dijon, France
Symposium honoring the Career of Prof. Wilse Robinson, ACS SWR Lubbock, TX
ACS National Meeting, Boston
Univ. of Minnesota, Physical Chemistry Seminar
Users meeting for Free Electron Lasers-Rheinberg, Germany
Conference on Size-selected clusters, Brand, Germany
Symposium honoring Nobelist John B. Fenn's 90th birthday, Richmond, VA
Wesleyan University, Department Colloquium

2006

APS Plyler prize award lecture, APS March meeting
Roger Miller symposium, APS March meeting
Concordia University, Chemistry colloquium, Montreal
Columbia University, Chemistry colloquium
Gordon research conference on Molecular and Ionic Clusters (Buelton)
ACS National meeting, Atlanta, symposium on electron-molecule collisions
ACS National meeting, San Francisco, (2 talks)
University of Wisconsin, Madison, Department colloquium
University of Pennsylvania, Physical chemistry seminar
University of Kentucky, Department Colloquium
Wayne State, Physical Chemistry Seminar
Gordon Conference on vibrational spectroscopy (Maine)
Gordon Conference on atomic and molecular interactions (New Hampshire)
Genesis Research Institute (Tokyo) conference on breakthroughs in cluster science
Jekyll Island conference on advances in clusters
Air Force office of Scientific research contractor's meeting
Symposium in honor of Roger Miller, University of North Carolina
Amherst College, Department seminar
Telluride workshop on water and hydrogen bonding
University of Pittsburgh, Physical chemistry seminar